

## Claims

- [c1] 1.A method for reactivating a deactivated carbonylation catalyst composition comprising a Group 8, 9 or 10 catalyst source, a Group 4 metal first inorganic co-catalyst source, and a Group 11 second inorganic co-catalyst source, which is present in a first liquid reaction mixture, said method comprising the following steps:
- an addition step, in which an aqueous solution comprising at least one protic acid source is added to said first liquid reaction mixture, resulting in a biphasic second liquid reaction mixture composed of an organic layer and an aqueous layer;
- a mixing step, whereby the biphasic second liquid reaction mixture is effectively agitated for a predetermined amount of time, followed by a settling stage in order to repartition the second liquid reaction mixture into the organic layer and the aqueous layer;
- a separation step, in which the organic layer of said second liquid reaction mixture is separated from said second liquid reaction mixture after a predetermined amount of time, resulting in an aqueous third liquid reaction mixture; and
- an evaporation step, wherein the volume of said aqueous third liquid reaction mixture is reduced by removing a predetermined amount of at least one component by evaporation at a predetermined temperature and pressure;
- wherein the carbonylation catalyst composition contained in the concentrated third liquid reaction mixture is more active, than the carbonylation catalyst composition contained in said first liquid reaction mixture, at carbonylating an aromatic hydroxy compound in a subsequent oxidative carbonylation reaction.
- [c2] 2.The method of claim 1, wherein the Group 8, 9 or 10 metal source is a palladium source.
- [c3] 3.The method of claim 2, wherein Group 4 metal first inorganic co-catalyst source is a titanium source and the Group 11 metal second inorganic co-

catalyst source is a copper source.

- [c4] 4.The method of claim 3, wherein the palladium source is present in an amount which is between about 1 ppm and 10000 ppm.
- [c5] 5.The method of claim 2, wherein at least part of the catalyst composition is insoluble in the first liquid reaction mixture.
- [c6] 6.The method of claim 1, wherein the first inorganic co-catalyst is present in an amount which is between about 1 equivalent and about 1000 equivalents versus the amount of Group 8, 9 or 10 metal source present.
- [c7] 7.The method of claim 1, wherein the second inorganic co-catalyst is present in an amount which is between about 1 equivalent and about 1000 equivalents versus the amount of Group 8, 9 or 10 metal source present.
- [c8] 8.The method of claim 1, wherein the carbonylation catalyst composition further comprises a salt source.
- [c9] 9.The method of claim 8, wherein the salt source is at least one member selected from the group consisting of an alkali halide, an alkaline-earth halide, a guanidinium halide, an ammonium halide, a phosphonium halide, a sulfonium halide, a carboxylate, an acetate, and a nitrate.
- [c10] 10.The method of claim 9, wherein the salt source is at least one member selected from the group consisting of lithium bromide, sodium bromide, potassium bromide, calcium bromide, magnesium bromide, tetrabutylammonium bromide, tetraethylammonium bromide, tetramethylammonium bromide, hexaethylguanidinium bromide, lithium chloride, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, tetrabutylammonium chloride, tetraethylammonium chloride, tetramethylammonium chloride, hexaethylguanidinium chloride, sodium acetate, and sodium nitrate.
- [c11] 11.The method of claim 10, wherein the salt source is present in an amount which is between about 1 equivalent and about 100000 equivalents versus

the amount of Group 8, 9 or 10 metal source present.

- [c12] 12.The method of claim 1, wherein the carbonylation catalyst composition further comprises at least one activating solvent.
- [c13] 13.The method of claim 12, wherein the activating solvent is one member selected from the group consisting of a polyether, and a nitrile.
- [c14] 14.The method of claim 13, wherein the activating solvent is present in an amount which is between about 0.1 weight % and about 50 weight % based on the total weight of the first liquid reaction mixture.
- [c15] 15.The method of claim 1, wherein the carbonylation catalyst composition further comprises at least one base source.
- [c16] 16.The method of claim 15, wherein the base source is at least one member selected from the group consisting of a basic oxide, a hydroxide, a mono-alkoxide, a poly-alkoxide, a monocyclic aryloxide, a polycyclic aryloxide, and a tertiary amine.
- [c17] 17.The method of claim 16, wherein the base source is at least one member selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, methyltributylammonium hydroxide, tetrabutylammonium hydroxide, sodium phenoxide, lithium phenoxide, potassium phenoxide, tetramethylammonium phenoxide, tetraethylammonium phenoxide, methyltributylammonium phenoxide, tetrabutylammonium phenoxide, triethyl amine, tributyl amine, and any mixtures thereof.
- [c18] 18.The method of claim 17, wherein the base source is present in an amount which is between about 1 equivalent and about 10000 equivalents versus the amount of Group 8, 9 or 10 metal source present.
- [c19] 19.The method of claim 1, wherein the first liquid reaction mixture comprises at least one member selected from the group consisting of an

aromatic carbonate, an aromatic hydroxy compound, a poly-aromatic hydroxy compound, a halogenated aromatic hydroxy compound, water, an aryl ether, and any mixtures thereof.

- [c20] 20.The method of claim 1, wherein the protic acid source is at least one member selected from the group consisting of hydrobromic acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, and any mixtures thereof.
- [c21] 21.The method of claim 20, wherein the amount of protic acid source present in the aqueous solution is between about 1 weight % and about 48 weight % based on the total weight of the aqueous solution.
- [c22] 22.The method of claim 21, wherein the addition of the aqueous solution is made by using at least one aliquot of an aqueous solution, wherein the amount of protic acid source present in each individual aliquot is different, and wherein the resulting second liquid reaction mixture contains two phases after all the aliquots have been added and agitation and settling are complete, and wherein the total volume of the aqueous solution added to the first liquid reaction mixture is between about 1 % and about 200 % of the volume of the first liquid reaction mixture.
- [c23] 23.The method of claim 22, wherein the extraction time, which is the total of agitation and settling time, after the addition of each aliquot is between about 0.1 minutes and 120 minutes, and the temperature of the liquid reaction mixture after the addition of each aliquot is between about 60 ° C and about 140 ° C during the extraction.
- [c24] 24.The method of claim 23, wherein the addition of the aqueous solution to the first liquid reaction mixture, and the first separation step are made by using an extraction column or a mixer followed by an extraction column.
- [c25] 25.The method of claim 1, wherein the addition of the aqueous solution to the first liquid reaction mixture, and the first separation step are made by using a mixer-settler vessel.

[c26] 26. The method of claim 1, wherein the separation of the aqueous layer from the second liquid reaction mixture is by decanting.

[c27] 27. The method of claim 1, wherein the third liquid reaction mixture comprises the Group 8, 9 or 10 metal source.

[c28] 28. The method of claim 1, wherein the volume of the third liquid reaction mixture is reduced by up to about 95% by evaporation.

[c29] 29. The method of claim 1, wherein the third liquid reaction mixture is evaporated almost up to dryness.

[c30] 30. The method of claim 1, wherein the temperature of third liquid reaction mixture during the evaporation step is between about 25 ° C and about 220 ° C, and the pressure during the evaporation step is between about  $1.3 \times 10^{-4}$  MPa and about 10 MPa.

31. A method for reactivating a deactivated carbonylation catalyst composition comprising a Group 8, 9 or 10 catalyst source a Group 4 metal first inorganic co-catalyst source and a Group 11 second inorganic co-catalyst source, which is present in a first liquid reaction mixture, said method comprising the following steps:

an optional first evaporation step, wherein the volume of the first liquid reaction mixture is reduced by removing a predetermined amount of at least one component by evaporation at a predetermined temperature and pressure;

a first addition step, in which an aqueous solution comprising at least one protic acid source is added to said first liquid reaction mixture, resulting in a biphasic second liquid reaction mixture composed of an organic layer and an aqueous layer;

a mixing step, whereby the biphasic second liquid reaction mixture is effectively agitated for a predetermined amount of time, followed by a settling stage in order to repartition the mixture into the organic layer and the aqueous layer;

a first separation step, in which the organic layer of said second liquid reaction mixture, is separated from said second liquid reaction mixture after a predetermined amount of time, to produce an aqueous third liquid reaction mixture;

an optional second evaporation step, wherein the volume of the aqueous third liquid reaction mixture is reduced by removing a predetermined amount of at least one component by evaporation at a predetermined temperature and pressure;

a second addition step, wherein a solution comprising at least one member selected from the group consisting of an activating solvent, an aromatic hydroxy compound, an aromatic carbonate, and mixtures thereof is added to the third liquid reaction mixture, forming a fourth liquid reaction mixture;

a third evaporation step, wherein the volume of the fourth liquid reaction mixture is reduced by removing a predetermined amount of at least one component by evaporation at a predetermined temperature and pressure;

a second separation step, in which any precipitate present in the fourth liquid reaction mixture after a predetermined amount of time is separated from the fourth liquid reaction mixture, therein producing a fifth liquid reaction mixture;

an third addition step, wherein at least one member selected from the group consisting of an aromatic hydroxy compound, a carbonate, an organic ligand source, a salt source, an activating solvent, a base source, and any mixtures thereof, is added to the fifth reaction mixture to produce a sixth liquid reaction mixture;

wherein the carbonylation catalyst composition contained in said sixth liquid reaction mixture is more active, than the carbonylation catalyst composition contained in said first liquid reaction mixture, at carbonylating an aromatic hydroxy compound in a subsequent oxidative carbonylation reaction.

[c32] 32.The method of claim 31, wherein the Group 8, 9 or 10 metal source is a palladium source.

[c33] 33.The method of claim 32, wherein Group 4 metal first inorganic co-

catalyst source is a titanium source and the Group 11 metal second inorganic co-catalyst source is a copper source.

- [c34] 34.The method of claim 33, wherein the palladium source is present in an amount which is between about 1 ppm and 10000 ppm.
- [c35] 35.The method of claim 31, wherein at least part of the catalyst composition is insoluble in the first liquid reaction mixture.
- [c36] 36.The method of claim 31, wherein the first inorganic co-catalyst is present in an amount which is between about 1 equivalent and about 1000 equivalents versus the amount of Group 8, 9 or 10 metal source present.
- [c37] 37.The method of claim 31, wherein the second inorganic co-catalyst is present in an amount which is between about 1 equivalent and about 1000 equivalents versus the amount of Group 8, 9 or 10 metal source present.
- [c38] 38.The method of claim 32, wherein the carbonylation catalyst composition further comprises a salt source.
- [c39] 39.The method of claim 38, wherein the salt source is at least one member selected from the group consisting of an alkali halide, an alkaline-earth halide, a guanidinium halide, an ammonium halides, a phosphonium halides, a sulfonium halides, a carboxylate, an acetate, and a nitrate.
- [c40] 40.The method of claim 39, wherein the salt source is at least one member selected from the group consisting of lithium bromide, sodium bromide, potassium bromide, calcium bromide, magnesium bromide, tetrabutylammonium bromide, tetraethylammonium bromide, tetramethylammonium bromide, hexaethylguanidinium bromide, lithium chloride, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, tetrabutylammonium chloride, tetraethylammonium chloride, tetramethylammonium chloride, hexaethylguanidinium chloride, sodium acetate, and sodium nitrate.
- [c41] 41.The method of claim 40, wherein the salt source is present in an amount

which is between about 1 equivalent and about 100000 equivalents versus the amount of Group 8, 9 or 10 metal source present.

[c42] 42.The method of claim 32, wherein the carbonylation catalyst composition further comprises at least one activating solvent.

[c43] 43.The method of claim 42, wherein the activating solvent is one member selected from the group consisting of a polyether, and a nitrile.

[c44] 44.The method of claim 43, wherein the activating solvent is present in an amount which between about 0.1 weight % and about 50 weight % based on the total weight of the first liquid reaction mixture.

[c45] 45.The method of claim 32, wherein the carbonylation catalyst composition further comprises at least one base source.

[c46] 46.The method of claim 45, wherein the base source is at least one member selected from the group consisting of a basic oxide, a hydroxide, a mono-alkoxide, a poly-alkoxide, a monocyclic aryloxide, a polycyclic aryloxide, and a tertiary amine.

[c47] 47.The method of claim 45, wherein the base source is at least one member selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, methyltributylammonium hydroxide, tetrabutylammonium hydroxide, sodium phenoxide, lithium phenoxide, potassium phenoxide, tetramethylammonium phenoxide, tetraethylammonium phenoxide, methyltributylammonium phenoxide, tetrabutylammonium phenoxide, triethyl amine, tributyl amine, and any mixtures thereof.

[c48] 48.The method of claim 47, wherein the base source is present in an amount which is between about 1 equivalent and about 10000 equivalents versus the amount of Group 8, 9 or 10 metal source present.

[c49] 49.The method of claim 31, wherein the first liquid reaction mixture



comprises at least one member selected from the group consisting of an aromatic carbonate, an aromatic hydroxy compound, a poly-aromatic hydroxy compound, a halogenated aromatic hydroxy compound, water, an aryl ether, and any mixtures thereof.

- [c50] 50.The method of claim of 31, wherein an aromatic hydroxy compound is removed from the first reaction mixture in the first evaporation step.
- [c51] 51.The method of claim 50, wherein the aromatic hydroxy compound is one member selected from the group consisting of phenol, 2-bromophenol, and 4-bromophenol.
- [c52] 52.The method of claim 51, wherein the amount of aromatic hydroxy compound removed from the first reaction mixture in the first evaporation step is between about 1 weight % and 75 weight % based on the total weight of the first reaction mixture.
- [c53] 53.The method of claim of 31, wherein an activating solvent is removed from the first reaction mixture in the first evaporation step.
- [c54] 54.The method of claim 53, wherein the activating solvent is a nitrile.
- [c55] 55.The method of claim 31, wherein the temperature of first liquid reaction mixture during the first evaporation step is between about 25 ° C and about 220 ° C, and the pressure of during the first evaporation step is between about  $1.3 \times 10^{-4}$  MPa and about 10 MPa.
- [c56] 56.The method of claim 31, wherein the protic acid source is at least one member selected from the group consisting of hydrobromic acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, and any mixtures thereof.
- [c57] 57.The method of claim 56, wherein the amount of protic acid source present in the aqueous solution is between about 1 weight % and about 48 weight % based on the total weight of the aqueous solution.

[c58] 58. The method of claim 56, wherein the addition of the aqueous solution is made by using at least one aliquot of an aqueous solution, wherein the amount of protic acid source present in each individual aliquot is different, and wherein the resulting second liquid reaction mixture contains two phases after all the aliquots have been added, and wherein the total volume of the aqueous solution added to the first liquid reaction mixture is between about 1 % and about 200 % of the volume of the first liquid reaction mixture.

[c59] 59. The method of claim 58, wherein the extraction time after the addition of each aliquot is between about 0.1 minutes and 120 minutes, and the temperature of the liquid reaction mixture after the addition of each aliquot is between about 60 ° C and about 140 ° C.

[c60] 60. The method of claim 59, wherein the addition of the aqueous solution to the first liquid reaction mixture is made by using an extraction column or a mixer followed by an extraction column.

[c61] 61. The method of claim 31, wherein the addition of the aqueous solution to the first liquid reaction mixture is made by using a mixer-settler vessel.

[c62] 62. The method of claim 31, wherein the second liquid reaction mixture is agitated by stirring.

[c63] 63. The method of claim 31, wherein the second liquid reaction mixture is agitated by sonication.

[c64] 64. The method of claim 31, wherein the separation of the aqueous layer from the second liquid reaction mixture in the first separation step is by decanting.

[c65] 65. The method of claim 32, wherein the third liquid reaction mixture comprises a Group 8, 9, or 10 metal source.

[c66] 66. The method of claim of 31, wherein at least one members selected from the group consisting of water, a protic acid source, an aromatic hydroxy compound, and an activating solvent is removed from the third liquid

reaction mixture in the second evaporation step.

- [c67] 67.The method of claim of 31, wherein the volume of the third liquid reaction mixture is reduced by up to about 95% by evaporation.
- [c68] 68.The method of claim 31, wherein the third liquid reaction mixture is evaporated up to almost dryness.
- [c69] 69.The method of claim 31, wherein the temperature of third liquid reaction mixture during the second evaporation step is between about 25 ° C and about 220 ° C, and the pressure of during the second evaporation step is between about  $1.3 \times 10^{-4}$  MPa and about 10 MPa.
- [c70] 70.The method of claim 31, wherein the activating solvent added during the second addition step is at least one member selected from the group consisting of a polyether, and a nitrile.
- [c71] 71.The method of claim 31, wherein the solution added during the second addition step further comprises an aromatic hydroxy compound.
- [c72] 72.The method of claim 71, wherein the aromatic hydroxy compound is phenol.
- [c73] 73.The method of claim of 31, wherein water is removed from the fourth reaction mixture in the third evaporation step.
- [c74] 74.The method of claim 73, wherein the amount of water removed is between about 1 weight % and about 99 weight % based on the total weight of the fourth reaction mixture.
- [c75] 75.The method of claim 31, wherein the temperature of fourth liquid reaction mixture during the third evaporation step is between about 25 ° C and about 220 ° C, and the pressure of during the third evaporation step is between about  $1.3 \times 10^{-4}$  MPa and about 10 MPa.
- [c76] 76.The method of claim 31, wherein the aromatic hydroxy compound in the third addition step is phenol.

- [c77] 77.The method of claim 31, wherein the ligand source in the third addition step is 2,4-pentanedionate.
- [c78] 78.The method of claim 31, wherein the precipitate removed in the second separation step is removed by filtration or centrifugation.
- [c79] 79.The method of claim 31, wherein the precipitate removed in the second separation step is a salt source.
- [c80] 80.The method of claim 79, wherein the salt source is a halide source.
- [c81] 81.The method of claim 80, wherein the halide source is at least one member selected from the group consisting of lithium bromide, sodium bromide, potassium bromide, calcium bromide, magnesium bromide, lithium chloride, sodium chloride, potassium chloride, calcium chloride, and magnesium chloride.
- [c82] 82.A method for reactivating a deactivated catalyst composition used in an oxidative carbonylation reaction of phenol to produce diphenyl carbonate using carbon monoxide and oxygen, said catalyst composition comprising a palladium source, a titanium source, a copper source, an alkali bromide, sodium hydroxide, and a polyether, contained in a first liquid reaction mixture comprising phenol, diphenyl carbonate, and water, said method comprising the following steps:
- an addition step, in which an aqueous solution comprising hydrobromic acid source is added to said first liquid reaction mixture, resulting in a biphasic second liquid reaction mixture composed of an organic layer and an aqueous layer;
  - a mixing step, whereby the biphasic second liquid reaction mixture is effectively agitated for a predetermined amount of time, followed by a settling stage in order to repartition the second liquid reaction mixture into the organic layer and the aqueous layer;
  - a separation step, in which the aqueous layer of said second liquid reaction mixture is separated from said second liquid reaction mixture after a

[illegible]

[c83]

83.A method for reactivating a deactivated catalyst composition used in an oxidative carbonylation reaction of phenol to produce diphenyl carbonate using carbon monoxide and oxygen, said catalyst composition comprising a palladium source, a titanium source, a copper source, an alkali bromide, sodium hydroxide, and a polyether, contained in a first liquid reaction mixture further comprising phenol, diphenyl carbonate, and water, said method comprising the following steps:

a first addition step, in which an aqueous solution comprising hydrobromic acid is added to said first liquid reaction mixture, resulting in a biphasic second liquid reaction mixture composed of an organic layer and an aqueous layer;

a mixing step, whereby the biphasic second liquid reaction mixture is effectively agitated for a predetermined amount of time, followed by a settling stage in order to re-partition the mixture into the organic layer and the aqueous layer;

Page 28 of 33

a predetermined amount of time, to produce an aqueous third liquid reaction mixture;

an optional second evaporation step, wherein the volume of the aqueous third liquid reaction mixture is reduced by removing a predetermined amount water by evaporation at a predetermined temperature and pressure;

a second addition step, wherein a solution comprising at least one member selected from the group consisting of a polyether, phenol, an aromatic carbonate, and any mixtures thereof is added to the third liquid reaction mixture, forming a fourth liquid reaction mixture;

a third evaporation step, wherein the volume of the fourth liquid reaction mixture is reduced by removing a predetermined amount of water by evaporation at a predetermined temperature and pressure;

a second separation step, in which components that precipitate from the concentrated fourth liquid reaction mixture after a predetermined amount of time are separated from the fourth liquid reaction mixture, therein producing a fifth liquid reaction mixture; and

an optional third addition step, wherein at least one member selected from the group consisting of phenol, 2,4-pentanedionate, an alkali bromide, a polyether, sodium hydroxide, and any mixtures thereof, is added to the fourth reaction mixture to produce a fifth liquid reaction mixture; and

wherein the carbonylation catalyst composition contained in said sixth liquid reaction mixture is more active, than the carbonylation catalyst composition contained is said first liquid reaction mixture, at carbonylating phenol in a subsequent oxidative carbonylation reaction.

[c84]

84.A method for reactivating a deactivated catalyst composition used in an oxidative carbonylation reaction of phenol to produce diphenyl carbonate using carbon monoxide and oxygen, said catalyst composition comprising a palladium source, a titanium source, a copper source, an alkali bromide, sodium hydroxide, and a nitrile solvent, contained in a first liquid reaction mixture further comprising phenol, diphenyl carbonate, and water, said method comprising the following steps:



wherein the carbonylation catalyst composition contained in said sixth liquid reaction mixture is more active, than the carbonylation catalyst composition contained in said first liquid reaction mixture, at carbonylating phenol in a subsequent oxidative carbonylation reaction.

Handwritten signature or initials, possibly "H. B. 21/".

CONFIDENTIAL